Atomic-Absorption Methods of Analysis Useful in Geochemical Exploration

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By F. N. WARD, H. M. NAKAGAWA, T. F. HARMS, *and* G. H. VanSICKLE

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A compilation of atomic-absorption methods yielding data on geologic materials useful in geochemical prospecting for ore deposits

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By F. N. WARD, H. M. NAKAGAWA, T. F. HARMS, and G. H. VANSICKLE

ABSTRACT

Atomic-absorption methods for determining 15 elements in soils and rocks are described in sufficient detail for use by nontechnical persons. These elements are silver, bismuth, cadmium, copper, lead, zinc, cobalt, nickel, calcium, lithium, sodium, potassium, gold (three methods), tellurium, and mercury. A few of these methods are modified from published procedures for use on geologic materials other than natural waters; the remaining ones have been developed in the U.S. Geological Survey laboratories.

Insofar as possible, sample dissolution is accomplished by digestion with hot nitric acid, but in certain samples, for example gold and tellurium, dissolution is accomplished by different combinations of hydrobromic acid and bromine, and in other samples, for example alkalis and calcium, dissolution is accomplished by perchloric, nitric, and hydrofluoric acid mixtures. Sample dissolution for the mercury determination is replaced by the application of heat to evolve the element or decompose its compounds. The methods differ in the judicious use of solvent extraction to separate the elements from possible interferences, to achieve a relatively uniform matrix, and to enrich the element above a threshold concentration amenable to atomic-absorption measurement.

Most of these procedures include short introductory statements of documentation and additional references as well as comments on the most common interferences when applied to soils and rocks.

INTRODUCTION

All the analytical methods described in this report are based on atomic-absorption spectrometry. They were devised primarily to increase the analytical capacity of the U.S. Geological Survey laboratories, especially to meet the needs of an expanded program to develop means to "identify exploration targets" as sources of certain strategic minerals (U.S. Geol. Survey, 1968). Some of the methods have been published (Huffman and others, 1966; Nakagawa and Harms, 1968; Nakagawa and Thompson, 1968; Thompson and others, 1968; Ward and Nakagawa, 1967); other methods are being processed for publication; and all the methods are still being investigated and improved not only to achieve greater sensitivity but also to permit application to a greater variety of geologic materials. The purpose in bringing the methods together in this report is to make them generally available to interested workers both in and out of the U.S. Geological Survey.

The principles of atomic-absorption measurement are relatively simple—so simple in fact that, as Kahn (1966) noted, they are "at least on the surface, too simple to be interesting." The sample for analysis is dispersed in a beam of energy, usually from a hollow-cathode lamp, and atoms in the ground state absorb the incident energy of certain discrete frequencies, which are called resonant frequencies. The absorption causes a decrease in emerging energy, and with suitable instrumentation the decrease can be measured relative to the incident beam or other reference and related to the concentration of the given element dispersed in the beam and ultimately to the amount of the element in a geologic sample.

Available instruments have a great many features, all of which are used at one time or another. Certain instruments measure the percentage of absorption relative to the incident energy, and others actually measure the absorbance (negative logarithm of transmission) by taking advantage of the fact that the voltage across a semiconductor diode is linear with respect to the direct current passing through the diode. Several commercial instruments offer built-in scale expansion, and others provide this feature by an accessory recorder. Some instruments with direct readouts provide for zero suppression which is advantageous for measuring concentrations in a given range, for example, from 3 to 8 ppm (parts per million).

Atomic-absorption methods are limited by the radiation sources, the sampling devices used to introduce the sample into the beam of radiation from the source, and the system—usually optical—for isolating the absorption frequencies.

Hollow-cathode lamps that provide emitted energy of well-defined frequencies are the most common radiation source. Other types of lamps, for example Osram, that emit a continuum were formerly used, especially for alkali determinations. Single-element hollow-cathode lamps have proved more useful than the multielement lamps. The single-element lamps not only have greater intensity and hence greater sensitivity, but also avoid the possibility of spectral interference due to closely spaced resonance frequencies, especially when cathodes are made from pure materials. Combinations of elements in multielement lamps are accordingly limited and often fail to satisfy the needs of more than one or two laboratories.

Initially the dispersion of monochromators ranged from 5 to 60 angstroms per millimeter, and over the range of a given monochromator the bandpass ranged from 15 to 60 A, but the need for efficient monochromators seemed unimportant because of the selectivity provided by the hollow-cathode lamps. However, the widespread application of atomic-absorption techniques to different materials and the increase in the number of elements determined on such

materials intensified the need for better resolution in the monochromator. This need was met by resonance detectors, introduced by Sullivan and Walsh (1965, 1966), which isolate the resonant radiation frequencies characteristic of the element being measured. Such resonant radiation is within a Doppler width of the excitation frequency, and for copper the width is of the order of 0.01 A. Amos (1967a) stated that "Observation of this radiation corresponds to a monochromator-detection system with a bandpass of about 0.02 Å."

These resonance detectors are based on the fact that ground-state atoms in an atomic vapor that is produced thermally or by a sputtering technique absorb resonant frequencies from an incident atomic spectrum. Atoms absorbing the resonant frequencies become excited for a finite time and during that time undergo reorientation, probably because of collisions. Ultimately they return to the ground state and in doing so emit isotropic radiation of the same resonant frequency as absorbed from the incident atomic spectrum.

In the assembled instrument the element being analyzed is atomized into the path of the atomic spectrum that is produced by a high-intensity hollow-cathode lamp, and the ground-state atoms absorb resonant frequencies proportional to the quantity of the element present. The variations in the absorbed frequencies govern the number of the atoms excited in the atomic vapor and hence the isotropic radiation from the atomic vapor. That radiation is detected by a photomultiplier placed at right angles to beam of the atomic spectrum and read out in the usual manner; however, phase-sensing detection techniques may be applied to the photomultiplier current to further enhance the signal-to-noise ratio and to improve the overall sensitivity.

The sampling device, which produces ground-state atoms of the element being measured, most commonly consists of a burner and nebulizer designed to atomize a solution of the element. For mercury because of the volatility of the element at ambient temperatures the need of a burner and nebulizer assembly is virtually eliminated. Infrequently other elements are volatilized by heat, and the vapor is passed into an absorption chamber. Venghiattis (1967) proposed to mix a sample with a solid fuel and oxidizer and to burn the pelletized mixture in the light path of a hollow-cathode lamp. His technique avoids clogging that may occur when solutions with gangue material are nebulized in the conventional burner, and it eliminates memory effects due to attack of burner by strong acid solutions; however, the flame of the fuel and oxidizer produces a continuum that tends to lower the sample-to-background ratio and the resulting sensitivity. Each of the above techniques is applicable to certain types of samples, but the most useful and by far the most common means of introducing a sample into the light path consists of nebulizing an aqueous solution

of the element into an acetylene-air flame. The aqueous solution is homogeneous as compared to the pelletized sample and oxidizer mixture, and it volatilizes at a uniform rate when properly nebulized.

The premix or laminar-flow burner and the total-consumption or diffusion-type burner are commonly used in atomic-absorption spectroscopy. The premix burner generally uses acetylene-air mixtures that burn quietly and reproducibly. The total-consumption burner generally uses hydrogen-air mixtures that under optimum conditions burn with an ear-splitting noise that even the best of engineering fails to suppress. Although the name total-consumption burner suggests a greater efficiency than the name premix, both burners are only about 5 percent efficient (Kahn, 1966). In the total-consumption burner the turbulent flow permits only the smallest droplets of nebulized sample solution to be dehydrated and burned, and in the premix burner the larger drops fall out in the mixing chamber and drain away, and again only the smallest droplets are dehydrated and burned.

The advantages of atomic-absorption methods over other analytical methods far outweigh the disadvantages (Amos, 1967b). Atomic-absorption methods are extremely sensitive (see definition of sensitivity on p. 7) for such elements as beryllium, copper, cobalt, magnesium, calcium, lithium, and zinc. They are also very precise—generally within ± 1 percent (Billings and Adams, 1964). Most commercial instruments used in these methods are equipped with direct readouts or can be so adapted, and they provide specificity and selectivity by the energy source—a hollow-cathode lamp or, more recently, a resonance detector as described above.

The disadvantages of atomic-absorption methods, aside from instrumental limitations, result primarily from the matrix that contains the element measured. These matrix problems consist of (1) interelement effects caused by the presence of different amounts of gangue elements initially present in or added to the sample during dissolution and (2) effects resulting from specific properties of the solvent or dispersant. Interference caused by interelement effects may be further defined as chemical, spectral, ionization, and molecular and particulate absorption.

Chemical interference includes compound formation in the flame—the compounds formed can differ in volatility as well as in ease of ionization.

Spectral interference occurs when the monochromator fails to resolve closely spaced resonant frequencies. This type of interference is less common in atomic-absorption spectroscopy than in flame emission spectroscopy, but may occur especially when multielement

hollow-cathode lamps are used (Jaworowski and Weberling, 1966) or when the cathodes of single-element lamps contain certain impurities that cause them to behave like multielement lamps. During assembly of regular multielement lamps, the manufacturer exercises a great deal of care to avoid combinations that cause spectral interference, but often fails to remove an impurity in a so-called pure metal used as a cathode.

Ionization interference is most common with alkali-metal determinations and is infrequently observed with the alkaline earths. The ease with which these elements ionize leaves fewer atoms in the ground state.

The interference due to molecular and particulate absorption is more often observed with aqueous solutions of high salt content (Angino and Billings, 1967). Originally David (1961) explained such interference by postulating that the particles of salt remaining after evaporation of small droplets in the flame actually impeded the incident radiation which appeared to the detector like absorbed light. The term "light scattering" was used to describe the phenomenon, but recently Koirtyohann and Pickett (1966) have shown that many such observations of the past are due not to light scattering but to molecular absorption, calcium being an outstanding example of a molecular absorber.

Illustrations of the interferences caused by these effects, and the attempts to nullify them, are described in the literature usually in connection with a specific need or problem. For example, Willis (1960a) adapted atomic-absorption spectroscopy to the determination of calcium in blood serum. He noted the depression of the calcium absorption by phosphate and suggested two different techniques to inhibit the depression: (1) adding ions such as strontium (II) or lanthanum (III) to compete with calcium ions for the phosphate, and (2) adding a compound such as the disodium salt of ethylenediaminetetraacetic acid to react with calcium and thus prevent its reaction with phosphate.

In another specific application P. B. Adams and W. O. Passmore (quoted by Slavin, 1965) added a buffer solution composed of the tetraammonium salt of ethylenediaminetetraacetic acid and lanthanum perchlorate to overcome the depression by aluminum on alkaline-earth determinations.

Interferences in atomic-absorption spectroscopy are not limited to depressive effects. Infrequently the effect is one of enhancement—as for example the interference of sodium in the determination of potassium—noted in natural waters by Fishman and Downs (1966), in brines by Billings (1965), and in serum by Willis (1960b). All these

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authors agree that the enhancement results from the ease of ionization of sodium and can be offset by equalizing the sodium content of both sample and standard or by the method of additions as used in flame photometry.

Despite the disadvantages and the extra steps required to compensate for the different kinds of interference described above, atomic-absorption techniques are comparable in accuracy with the widely used colorimetric procedures, as shown by the data in table 1.

TABLE 1.—*Determination of copper content of soils, in parts per million, by colorimetric and atomic-absorption methods*

Sample	Colorimetry (in 1964)	Atomic absorption (in 1967)
1	10	12
2	15	14
3	20	20
4	20	24
5	30	30
6	60	68
7	150	150

Another advantage of atomic-absorption techniques is the number of elements that can be determined from a single solution of a given sample, as shown by the data in table 2. All these elements were determined from a single dilute nitric acid solution of the ash.

TABLE 2.—*Atomic-absorption analysis, in parts per million, of fir ash*

Sample	Copper	Lead	Bismuth	Zinc	Silver
1	60	60	30	1, 500	<2
2	70	40	40	2, 200	2
3	90	30	<20	2, 800	2
4	80	30	30	2, 000	<2
5	70	30	20	1, 400	<2
6	180	30	20	3, 600	6

The accuracy, speed, and simplicity of the proposed atomic-absorption methods are readily apparent. Moreover, these methods are obviously most useful when large numbers of samples need to be analyzed for a relatively few elements to establish gross differences in composition that can be related to geologic controls and features.

These analytical methods resemble the colorimetric methods used in geochemical exploration (Ward and others, 1963) in design objectives such as speed, simplicity, and accuracy commensurate with the problem.

The minimum content of elements detectable by each of the methods described below and the content detectable by other analytical

methods found useful in geochemical exploration are given in table 3, together with the average content of the same elements in soils, basalts, and granites.

TABLE 3.—*Minimum concentrations detectable by methods useful in geochemical exploration and average contents of the elements in soils, basalts, and granites*

[------, not determined]

Element	Sensitivity of method (ppm)			Average content (ppm, except as noted)		
	Colorimetric[1]	Spectrographic[1] d-c arc	Atomic absorption[2]	Soils[1]	Basalts[3]	Granites[3]
Bismuth	10	10	10	[4] 0.2	0.15	0.18
Calcium	------	------	5	------	[5] 6.72	[5] 1.58
Cadmium	------	20	.2	.5	.2	.2
Cobalt	10	10	4	8	48	1
Copper	10	5	.1	20	100	10
Gold	------	------	.005	------	.004	.004
Lead	25	10	1	30	5	20
Lithium	------	------	.5	------	10	30
Mercury	2	------	.001	.01	.08	.08
Nickel	25	5	4	40	150	.5
Potassium	------	------	2.5	------	[5] .83	[5] 3.34
Silver	------	1	1	.1	.1	.04
Sodium	------	------	2.5	------	[5] 1.94	[5] 2.77
Tellurium	------	------	.2	------	------	------
Zinc	25	200	.5	50	100	40

[1] From Ward, Lakin, Canney, and others (1963).
[2] Present report.
[3] From Taylor (1964).
[4] Value given in crustal abundance (Mason, 1958).
[5] Values in percent.

The sensitivities given in table 3 are of concentrations expressed in parts per million that produce a positive result with the colorimetric methods, a definite line on a photographic film with the spectrographic methods, or a distinguishable signal above background on an atomic-absorption instrument.

All the methods described in this report have been adapted to the model 303 and some to both models 303 and 290 atomic-absorption instruments, which are marketed in the United States by the Perkin-Elmer Corp. Other instruments manufactured in the United States and elsewhere are equally useful, and the fact that the name of an instrument is used in this report does not constitute a written or implied endorsement of that instrument.

The sensitivity of an atomic-absorption method is defined by most workers (for example, Slavin, 1968) as the concentration of the element in solution that produces 1 percent absorption. Our values are somewhat greater and are determined as in the following paragraph.

When the readout meter of a model 290 instrument is set for full-scale deflection while atomizing a 10-ppm standard solution, we read signals of not less than 2.5 scale divisions which corresponds to a

solution of 0.25 ppm. If the instrument is unsteady we cut off at 5 scale divisions or 0.5 ppm of element being determined. Infrequently the lowest standard differs from the sensitivity given in table 3 because of particular conditions. In all cases, however, the sensitivities given in table 3 and discussed under the individual elements are established as above.

We present a general procedure for sample attack with boiling nitric acid when analyzing for silver, bismuth, cadmium, lead, copper, zinc, cobalt, and nickel; the specific directions for preparation of working standard solutions; instrumental parameters for Perkin-Elmer atomic-absorption instruments models 303 and 290; and a brief discussion of interferences, special precautions, warnings, or reasons for certain steps. Initially we relied heavily on the instrumental parameters furnished in the Perkin-Elmer instruction book (Perkin-Elmer Corp., 1966) and altered them where necessary to meet our needs.

All the determinations described in this report, except those for tellurium and mercury, can be made on the model 290 spectrophotometer, and where the procedures described include operating conditions for only the model 303, the authors mean simply that the model 290 has not been used enough for the particular analysis to establish such parameters.

Boiling nitric acid is used to effect sample dissolution in eight of the procedures given here. The boiling nitric acid is used because it is less dangerous than hot perchloric acid, especially under field conditions and in the hands of relatively untrained personnel, and because the sample solution of about 7 *M* nitric acid is less corrosive on the metal parts of the burner-nebulizer assembly than aqua regia, for example. Moreover, the significant trace amounts of metal in exploration have quite likely been introduced into the rocks by hydrothermal or other genetic processes, and such metals are easily solubilized by boiling nitric acid. Background amounts of metals such as copper and zinc in crystal lattices of silicates are less significant in exploration, and the need to solubilize them is not as important in exploration as in abundance and distribution studies. Few, if any, strong geochemical anomalies will be missed because of the use of boiling nitric acid for sample dissolution.

We also present a general procedure of sample attack with nitric, perchloric, and hydrofluoric acids when analyzing for calcium, lithium, potassium, and sodium, followed by specific directions, instrumental parameters, and precautions as stated above.

We also include three methods for determining gold, one method for tellurium, and a nonsolution-of-sample procedure for determining background concentrations of mercury.

Caution.—Because of the varied experience of persons who may use these procedures, we emphasize that most chemical reagents are poisonous and require care in handling, especially around open flames, bottles, and the like. Further caution and a complete discussion of possible hazards are given by Ward, Lakin, Canney, and others (1963, p. 5).

ATOMIC-ABSORPTION DETERMINATION OF THE CONSTITUENTS

SILVER, BISMUTH, CADMIUM, LEAD, COPPER, ZINC, COBALT, AND NICKEL IN ROCKS AND SOILS

GENERAL PROCEDURE

REAGENTS AND EQUIPMENT

Nitric acid, concentrated, ACS (American Chemical Society).

Water, metal-free, demineralized—prepared by passing tap or, preferably, distilled water through a demineralizer cartridge or other resin bed. (In this bulletin water always means metal-free or demineralized water.)

Culture tubes, 16- by 150-millimeter, calibrated at 10 milliliters.

Magnets, Teflon-covered, ½- by ⁵⁄₁₆-inch. (Infrequently, the Teflon develops holes or becomes porous exposing magnets to hot acid attack, resulting in contamination of sample solution.)

Magnetic stirrer and hotplate, fitted with aluminum heating block drilled to hold culture tubes.

Centrifuge, desirable but not necessary.

Spectrophotometer, atomic-absorption.

SAMPLE DIGESTION

Place 1.0 gram of powdered rock or soil in a 16- by 150-mm test tube. Add one small Teflon-covered magnet and 5 ml concentrated nitric acid. Place tube and contents in one hole of an aluminum heating block fitted on top of hotplate equipped with magnetic stirrer. Start agitation of sample-acid mixture and heat to boil. Continue boiling and stirring for 30 minutes. Remove tube from block, allow solution to cool slightly, add 5 ml water, heat mixture to boil and then allow to cool. Make up to 10-ml mark with concentrated nitric acid. Mix and centrifuge or filter.

ESTIMATION

Zero instrument with 1:1 nitric acid and atomize the supernatant liquid or filtrate in an atomic-absorption spectrophotometer. Read the

absorbance and convert to concentration in atomized solution as directed below for the particular instrument. Calculate results as follows:

$$\text{Ppm in sample} = (\mu g/\text{ml in solution}) \times 10.$$

INSTRUMENT CALIBRATION

Note.—The following directions are complementary to the detailed directions included in the different instrument manuals, which the analyst should study before attempting any atomic-absorption determinations.

Model 303 using × 1 scale expansion.—Atomize three or more working standard solutions, and manually measure the percent absorption. Refer to the conversion table furnished with the instrument to change percent absorption to absorbance, and prepare a standard curve by plotting concentrations of the working standard solutions against the corresponding absorbance values.

If the conversion table is not available, the percentage of absorption can be converted to absorbance as follows:

$$\text{Absorbance} = -\log\left[1 - \frac{\text{percentage of absorption}}{100}\right].$$

For example, when percentage of absorption is 42 as measured on model 303, then

$$\begin{aligned}\text{absorbance} &= -\log\,[1-0.42] = -\log\,[0.58]\\ &= -[-0.237] = 0.237.\end{aligned}$$

If the model 303 is equipped with digital concentration readout (DCR), atomize the largest working standard solution and set readout at the concentration being atomized as directed in the manual for the readout. This accessory performs automatically all the operations shown above for manual operation; and, if the system responds linearly—not necessarily required but preferable—then lesser concentrations can be read out directly.

Model 290.—Atomize the largest working standard solution and set the meter to maximum deflection—usually 100. With linearly responding systems the meter deflection is proportional to the concentration of the element being atomized, and direct readout is possible, thus avoiding setting up standard curves and the like.

If the sensitivity is inadequate to achieve full-scale deflection with the largest working standard solution of the element being determined, set the meter, which on the model 290 is linear with respect to absorbance, at some convenient number and use only the part of the scale from zero to that number. For example, set the meter at 50 and use only the part of the scale from 0 to 50.

SPECIFIC PROCEDURES

SILVER

The atomic-absorption method given here is a modification of one described by Huffman, Mensik, and Rader (1966), who reported that as little as 1 ppm and as much as 9,000 ppm (about 0.03 to 250 troy ounces per ton) silver can be determined without preliminary separation from high concentrations of such elements as iron, nickel, copper, bismuth, arsenic, and antimony.

A greater sensitivity is achieved in the modified procedure described here by taking advantage of the scale expansion provided in the model 303 atomic-absorption instrument. As little as 0.02 ppm silver can be measured, which in the procedure given here corresponds to 0.1 ppm in the soil or rock sample. Such concentration is only an order of magnitude greater than the crustal abundance; and if the sample size is doubled and other reagents are held constant, a sensitivity of 0.05 ppm is achieved permitting the detection of anomalous amounts in the earth's crust.

The silver in the rock or soil sample is dissolved in hot concentrated nitric acid stabilized with mercuric nitrate (Rubeska and others, 1967) and subsequently diluted with water to decrease the acid concentration to about 7 *M*. The silver content is measured by atomic-absorption spectrometry using working standard solutions for instrument calibration and instrumental parameters as given below.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are given below.

Mercuric nitrate reagent: Dissolve 150 mg mercuric nitrate in 500 ml concentrated nitric acid.

Standard solutions:

Silver standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Dissolve 0.158 g silver nitrate in 100 ml 1:1 nitric acid.
B	100	Prepare fresh by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	50	Prepare fresh by diluting 50 ml of *B* to 100 ml with 1:1 nitric acid.
D	10	Prepare fresh by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.
E	5	Prepare fresh by diluting 50 ml of *D* to 100 ml with 1:1 nitric acid.
F	0. 5	Prepare fresh by diluting 10 ml of *E* to 100 ml with 1:1 nitric acid.

Working silver standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of silver in parts per million, dilute 5 ml of the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
0.05	*F.*
0.5	*E.*
1.0	*D.*
5.0	*C.*

Optimum working range with model 303:
  Manual (× 1), 0.2 through 5.0 ppm.
  (× 5), 0.02 through 0.5 ppm.
  DCR, 0.02 through 5.0 ppm.

Operating conditions for model 303:
  Wavelength, 3280 A.
  Source, hollow cathode.
  Lamp current, 12 ma (milliampere).
  Range, ultraviolet.
  Slit, 4.
  Boling burner:
    Air pressure, 30 psi (pounds per square inch).
    Acetylene pressure, 8 psi.

Sample digestion: Place 1 g of powdered rock or soil in a 16- by 150-mm test tube. Add 1 small Teflon-covered magnet and 5 ml of mercuric nitrate reagent. Place tube and contents in the hole of an aluminum heating block and continue as in "General procedure" (p. 9).

Estimation: Refer to "General procedure" (p. 9).

Discussion: After sample dissolution and collection of the silver in an acid solution the actual measurement by atomic-absorption spectrometry is relatively easy and free of interferences (Slavin, 1968). H. W. Lakin (oral commun., 1968) observed that traces of chloride in the reagents and the water caused precipitation of the silver. A similar observation was made by Rubeska, Sulcek, and Moldan (1967), who reasoned that mercury would remove the interference by forming a less dissociated compound with chloride. The procedure given above includes addition of mercury as the nitrate.

BISMUTH

The atomic-absorption determination of bismuth in altered rocks is discussed in detail by Ward and Nakagawa (1967). Sample dis-

solution with boiling nitric acid is effective on bismuth minerals such as bismuthinite and certain associated minerals such as tetradymite and galena. Without any enrichment or preconcentration as little as 10 ppm of bismuth is measured with a relative standard deviation of about 10 percent. This sensitivity has to be improved to detect anomalous amounts of bismuth inasmuch as the crustal abundance is of the order of 0.01–0.1 ppm. Techniques for improving the sensitivity are being investigated, but meanwhile the method has proved useful in pinpointing areas of possible economic potential.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are tabulated below.

Standard solutions:

Bismuth standard stock solution	Concentration (ppm)	Procedure
A	1,000	Dissolve 0.5 g bismuth metal in 500 ml concentrated nitric acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	50	Prepare by diluting 50 ml of *B* to 100 ml with 1:1 nitric acid.
D	10	Prepare daily by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.

Working bismuth standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of bismuth in parts per million, dilute 5 ml of the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
1	*D*.
5	*C*.
10	*B*.

Optimum working range with model 303:

Manual (× 1), 1 through 10 ppm.

DCR, 1.0 through 10 ppm.

Operating conditions for instruments:

	Model 303	*Model 290*
Wavelength (counter)	2230 A	98. 5
Source	Hollow cathode	Hollow cathode
Lamp current ma	30	12
Slit	3	7 A
Boling burner:		
Air pressure psi	30	30
Acetylene pressure psi	8	8

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Sample digestion: Refer to "General procedure" (p. 9).
Estimation: Refer to "General procedure" (p. 9).
Discussion: Billings (1965) reported that "calcium interferes strongly" with bismuth; although we have not observed such interference with rocks and soils, we confirmed his report during the analysis of samples of alfalfa collected in Arizona and Utah. The air-dried alfalfa was ignited at 450° C overnight and the resulting ash was leached with boiling nitric acid. The acid solution of each sample was atomized into a flame, and the absorption of the 2230-angstrom bismuth line in the presence of about 15,000 ppm calcium corresponded to about 70–80 ppm bismuth in the ash. The ash contains less than 10 ppm bismuth when analyzed by a colorimetric procedure.

CADMIUM

The atomic-absorption determination of cadmium in rocks and soils is discussed in detail by Nakagawa and Harms (1968). Without any preconcentration as little as 0.2 ppm of cadmium in a soil or rock is measured with reasonable precision. The crustal abundance of cadmium is of the same order of magnitude and thus any anomalous amount in a rock is detectable by the procedure.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are tabulated below.

Standard solutions:

Cadmium standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Dissolve 0.1142 g cadmium oxide in 100 ml 1:1 nitric acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	10	Prepare by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.
D	1	Prepare daily by diluting 10 ml of *C* to 100 ml with 1:1 nitric acid.
E	0. 5	Prepare daily by diluting 50 ml of *D* to 100 ml with 1:1 nitric acid.
F	0. 2	Prepare daily by diluting 20 ml of *D* to 100 ml with 1:1 nitric acid.

Working cadmium standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of cadmium

in parts per million, dilute the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
0.02	5 ml of *F*.
0.05	5 ml of *E*.
1.0	Use *D* above.
3.0	15 ml of *C*.

Optimum working range with model 303:
Manual, 0.02 through 1 ppm or 0.5 through 3 ppm.
DCR, 0.02 through 3 ppm.
Operating conditions for instruments:

	Model 303	*Model 290*
Wavelength (counter)	2288 A	109
Source	Hollow cathode	Hollow cathode
Lamp current ma	6	3
Slit	4	7 A
Boling burner:		
Air pressure psi	30	30
Acetylene pressure psi	8	8

Sample digestion: Refer to "General procedure" (p. 9).
Estimation: Refer to "General procedure" (p. 9).
Discussion: The method has been successfully used to determine trace amounts of cadmium in zincite, sphalerite, and oxidized ores with no observed interference. The selectivity and sensitivity are adequate for the analysis of cadmium in geologic materials, and thus, this method can relieve the scarcity of data heretofore caused by the lack of a selective analytical procedure.

LEAD

The emission from the older lead hollow-cathode lamps used in most commercial atomic-absorption instruments was low because the discharge occurred on the outside and the inside of the hollow cathode. The discharge on the outside contributed little to the emitted energy which originated primarily in the cathode cavity (Manning and Vollmer, 1967). Accordingly, the relative detection limit achieved for lead was much less than that for zinc or copper. Despite this drawback, atomic-absorption techniques have been widely used on a variety of geologic and metallurgical materials.

The new shielded lamps have an insulating shield positioned around the cathode so as to restrict the discharge to the cathode cavity and thereby to increase the emitted energy at a given lamp current. The increased emission results in greater sensitivity, other factors being equal.

Background amounts of lead in rocks and soils are of the order of 15–20 ppm, and the procedure given here with a sensitivity of 0.1 ppm is more than adequate to measure such amounts. In fact the good sensitivity and relatively high background allow one to dilute the sample solution appreciably to achieve a uniform matrix and to nullify possible interferences.

The accuracy of the lead determinations in the different rocks is established by comparing lead contents determined by the proposed atomic-absorption method with lead contents determined by independent methods such as colorimetry and emission spectrography. The data for such a comparison are shown in table 4.

TABLE 4.—*Lead content, in parts per million, of rocks and minerals*

Sample	Material	Atomic absorption [1]	Colorimetry [2]	Spectrography [3]
R4A	Hornblende	13	7	<10
2A	Sandstone	14	10	<10
7A	Basalt	14	16	10
5A	Quartz monzonite	17	20	20
3A	Biotite	19	24	20
8A	Dolomite	22	13	<10
6A	Granite	23	35	20

[1] Average of five determinations by procedure described in this report.
[2] Average of 10 colorimetric measurements after sample digestion with $HF–HClO_4–HNO_3$.
[3] Semiquantitative three-step procedure.

The agreement of values obtained by the three independent methods is ample evidence of the accuracy of the proposed method.

The repeatability of the atomic-absorption method is established by several separate determinations on different kinds of rocks. The highest and lowest values obtained for lead in several rock and mineral samples, as well as the confidence limits at the 95-percent level and the relative standard deviations, are shown in table 5.

TABLE 5.—*Repeatability of lead determinations on rocks and minerals*

[Average of five determinations]

Sample	Material	Lead (ppm)		Mean and confidence limits at 95-percent level	Relative standard deviation (percent)
		Low	High		
R4A	Hornblende	10	16	13.2±2.9	17.4
2A	Sandstone	12	16	13.6±2.1	12.5
7A	Basalt	12	16	14.0±1.8	10.0
5A	Quartz monzonite	14	18	16.8±2.2	10.7
3A	Biotite	18	20	19.2±1.4	5.7
8A	Dolomite	20	24	22.4±2.1	7.6
6A	Granite	22	24	22.8±1.4	4.8

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are tabulated below.

Standard solutions:

Lead standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Dissolve 1.6 g lead nitrate in 1,000 ml of 1:1 nitric acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	10	Prepare daily by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.

Working lead standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of lead in parts per million, dilute the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
2	10 ml of *C*.
10	Use *C* above.
30	15 ml of *B*.

Optimum working range with model 303:
Manual (× 1), 1 through 30 ppm.
(× 5), 0.1 through 3 ppm.
DCR, 0.1 through 10 ppm.

Operating conditions for instruments:

	Model 303	*Model 290*
Wavelength (counter)	2170 A	205
Source	Hollow cathode	Hollow cathode
Lamp current ma	30	15
Slit	4	7 A
Boling burner:		
Air pressure psi	30	30
Acetylene pressure psi	8	8

Sample digestion: Refer to "General procedure" (p. 9).
Estimation: Refer to "General procedure" (p. 9).

COPPER

Copper is perhaps the easiest of all the metals to determine by atomic-absorption spectrometry, and the simplicity of the measurement as well as the freedom from interferences prompted Slavin (1968) to observe that it is most often used to check instrument performance. Instrumental changes do little "to degrade the copper

analysis." Further evidence of its ease of determination is provided by the success of Belt (1964) in copper determinations in complex geologic materials and of Strasheim, Strelow, and Butler (1960) in ores.

The crustal abundance of copper is of the order of 10–20 ppm and the method described here has a sensitivity of about 0.1 ppm—more than enough to determine background amounts and anomalous concentrations.

The copper of exploration significance found in rocks and soils is due mostly to weathered products of primary minerals and is readily soluble in hot nitric acid. The effectiveness of such a treatment on a suite of rocks and minerals and a measure of the accuracy achieved are shown by comparing the copper contents obtained by the atomic-absorption procedure with those obtained by established procedures—colorimetry (Ward and others, 1963) and semiquantitative spectrography (Myers and others, 1961). The results are given in table 6.

TABLE 6.—*Copper content, in parts per million, of rocks and minerals*

Sample	Material	Atomic absorption [1]	Colorimetry [2]	Spectrography [3]
R6A	Granite	2.4	4	5
2A	Sandstone	3.9	6	20
8A	Dolomite	6.4	6	5
5A	Quartz monzonite	6.8	8	10
4A	Hornblende	37	31	50
3A	Biotite	40	38	50
7A	Basalt	57	50	50

[1] Average of five determinations by procedure described in this report.
[2] Average of 10 colorimetric measurements after sample digestion with $HF-HClO_4-HNO_3$.
[3] Semiquantitative three-step procedure.

The good agreement of the results obtained by the different analytical techniques on such a wide variety of rocks and minerals is ample evidence of the accuracy of the atomic-absorption method.

The repeatability of the atomic-absorption procedure was established by making five separate determinations of the copper content of the suite of rocks and minerals (table 6). The lowest and highest values obtained, as well as the confidence limits at the 95-percent level and the relative standard deviation, are shown in table 7.

The relative standard deviation for rocks containing about 6 ppm copper is approximately 10 percent, which compares favorably with that reported by Belt (1964) for similar copper concentrations in a granite.

TABLE 7.—*Repeatability of copper determinations on rocks and minerals*

[Average of five determinations]

Sample	Material	Copper (ppm)		Mean and confidence limits at 95-percent level	Relative standard deviation (percent)
		Low	High		
R6A	Granite	2.0	2.8	2.4±0.7	19
2A	Sandstone	3.6	4.4	3.9±0.4	9
8A	Dolomite	6.0	7.2	6.4±0.8	10
5A	Quartz monzonite	6.0	7.6	6.8±0.9	11
4A	Hornblende	36.0	38.0	37.4±1.0	2.1
3A	Biotite	39.0	41.0	40.3±1.7	3.3
7A	Basalt	57.0	58.0	57.2±0.4	0.6

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are tabulated below.

Standard solutions:

Copper standard stock solution	Concentration (ppm)	Procedure
A	100	Dissolve 0.1964 g of clear uneffloresced crystals of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 500 ml of 1:1 nitric acid.
B	10	Prepare daily by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	1	Prepare daily by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.

Working copper standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of copper in parts per million, dilute the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
0.2	10 ml of *C*.
1	Use *C* above.
2	10 ml of *B*.
5	25 ml of *B*.

Optimum working range with model 303:

Manual (× 1), 0.5 through 10 ppm.

(× 5), 0.05 through 1 ppm.

DCR, 0.01 through 5.0.

Operating conditions for instruments:

	Model 303	*Model 290*
Wavelength (counter)	3248 A	280
Source	Hollow cathode	Hollow cathode
Lamp current ma	15	5
Slit	4	7 A
10-cm burner:		
Air pressure psi	30	30
Acetylene pressure psi	8	8

Sample digestion: Refer to "General procedure" (p. 9).
Estimation: Refer to "General procedure" (p. 9).

ZINC

The determination of zinc by atomic-absorption spectroscopy appears easy at first glance. The crustal abundance is of the order of 100 ppm and with a sensitivity of 0.5 ppm one can make several-fold dilutions of sample solution and thereby nullify possible matrix and spectral interferences.

The accuracy of zinc determinations on different kinds of rocks is established by comparing the results obtained by the proposed atomic-absorption method with those obtained by other tested methods referred to above. The data are shown in table 8.

TABLE 8.—*Zinc content, in parts per million, of rocks and minerals*

[------, not determined]

Sample	Material	Colorimetry [1]	Atomic absorption [2]	Atomic absorption [3]
R2A	Sandstone	11	4.4	------
8A	Dolomite	17	11.1	23
5A	Quartz monzonite	75	49.5	------
4A	Hornblende	100	20	85
3A	Biotite	100	164	------
6A	Granite	100	128	80
7A	Basalt	120	32	120

[1] Average of 10 or more colorimetric measurements after sample digestion with $HF-HClO_4-HNO_3$.
[2] Average of five determinations by procedure described in this report.
[3] Single determination by atomic absorption after sample digestion with $HF-HNO_3$.

The digestion of the samples with hot concentrated nitric acid is adequate for solubilizing trace amounts of zinc in many rock types, but remarkably inadequate for rocks in which the metal is possibly bound in a silicate lattice such as in a rock containing hornblende. In fact, most atomic-absorption procedures for determining zinc in geologic materials call for the use of a mixture of hydrofluoric acid and some other acid to insure breakdown of the silicates. However, the fact that the simpler digestion with boiling nitric acid is effective in revealing the presence of anomalous amounts of zinc warrants its continued use in place of the more drastic treatment involving hydrofluoric acid.

The repeatability of the proposed method is shown by the data in table 9. The repeatability of the zinc determinations on rocks such as the quartz monzonite as measured by the relative standard deviation is comparable to that observed by Belt (1967) for similar rocks. It is not good, possibly due to incomplete solution, but is deemed adequate for geochemical exploration.

TABLE 9.—*Repeatability of zinc determinations on rocks and minerals*
[Average of five determinations]

Sample	Material	Zinc (ppm)		Mean and confidence limits at 95-percent level	Relative standard deviation (percent)
		Low	High		
R2A	Sandstone	3. 6	6. 4	4. 4± 1. 4	25. 0
8A	Dolomite	10. 4	11. 8	11. 1± 0. 6	4. 5
4A	Hornblende	18. 4	20. 8	20. 0± 1. 4	5. 5
7A	Basalt	29. 8	33. 8	32. 2± 2. 0	4. 9
5A	Quartz monzonite	47. 2	50. 2	49. 5± 2. 1	3. 4
6A	Granite	116. 0	164. 0	128. 0±31. 0	19. 3
3A	Biotite	126. 0	246. 0	164. 0±62. 0	30. 2

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are tabulated below.

Standard solutions:

Zinc standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Dissolve 1 g zinc metal in 1 liter of 1:1 nitric acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	10	Prepare daily by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.
D	1	Prepare daily by diluting 10 ml of *C* to 100 ml with 1:1 nitric acid.
E	0. 5	Prepare daily by diluting 50 ml of *D* to 100 ml with 1:1 nitric acid.

Working zinc standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of zinc in parts per million, dilute the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
0. 05	5 ml of *E*.
0.1	5 ml of *D*.
0.2	10 ml of *D*.
1	Use *D* above.
3	15 ml of *C*.

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Optimum working range with model 303:
Manual (× 1), 0.2 through 3.0 ppm.
(× 5), 0.05 through 0.2 ppm.
DCR, 0.05 through 3.0 ppm.
Operating conditions for model 303:
Wavelength, 2138 A.
Source, hollow cathode.
Lamp current, 15 ma.
Slit, 4.
Boling burner:
Air pressure, 30 psi.
Acetylene pressure, 8 psi.
Sample digestion: Refer to "General procedure" (p. 9).
Estimation: Refer to "General procedure" (p. 9).
Discussion: A detailed study by Ward and Nakagawa (1969) confirmed several kinds of interference such as the effect of acid concentration noted by Gidley and Jones (1960) and the effect of sodium, potassium, magnesium, and iron noted by Billings (1965). These effects are in addition to the problem of sample dissolution discussed above.

COBALT

The following procedure is simple and useful in determining the small amount of easily dissolved cobalt in soils and rocks. The practical sensitivity of the procedure is of the order of 2–4 ppm depending on the size of the sample used. Such sensitivity is enough to measure background amounts ranging from 1 to 50 ppm and more than adequate to detect anomalous amounts.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are tabulated below.

Standard solutions:

Cobalt standard stock solution	Concentration (ppm)	Procedure
A	1,000	Dissolve 1.97 g cobalt chloride ($CoCl_2 \cdot 6H_2O$) in 500 ml of 1:1 nitric acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	10	Prepare daily by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.
D	5	Prepare daily by diluting 50 ml of *C* to 100 ml with 1:1 nitric acid.
E	1	Prepare daily by diluting 10 ml of *C* to 100 ml with 1:1 nitric acid.

Working cobalt standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of cobalt in parts per million, dilute the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
0.2	10 ml of *E*.
0.5	5 ml of *D*.
1	Use *E* above.
3	15 ml of *C*.
5	Use *D* above.

Optimum working range with model 303:
  Manual (× 1), 0.2 through 5 ppm.
  DCR, 0.2 through 5 ppm.
Operating conditions for instruments.

	Model 303	*Model 290*
Wavelength (counter)	2407 A	131. 5
Source	Hollow cathode	Hollow cathode
Lamp current ma	30	10
Slit	3	2 A
Boling burner:		
Air pressure psi	30	30
Acetylene pressure psi	8	8

Sample digestion: Place 0.5 g of powdered rock or soil in a 16- by 150-mm test tube and proceed as in "General procedure" (p. 9).
Estimation: Refer to "General procedure" (p. 9).
Discussion: In silicate rocks the atomic-absorption determination of cobalt is generally free of interferences (Billings, 1963; Billings and Adams, 1964), but in carbonates the determination is affected by molecular absorption of the dissolved calcium (Angino and Billings, 1967, p. 44). The determination in both silicates and carbonates presented no special difficulties for Montagut-Buscas, Obiols, and Rodriquez (1967). However, several published procedures include lengthy and perhaps tedious separation and concentration steps prior to atomizing a cobalt solution in an atomic-absorption instrument; therefore, the generalized statements above may in fact have only limited support.

NICKEL

The atomic-absorption determination of nickel is relatively easy, although a monochromator with a narrow spectral slit width, about 2 A, is needed to take advantage of the most sensitive resonant line at 2320 A. The practical sensitivity of the method included here is similar to that of cobalt, 2–4 ppm, and is adequate to measure the background amount which for the most part is slightly greater than

the 1- to 50-ppm range given for cobalt (p. 22). Certainly the sensitivity is more than necessary to detect anomalous amounts.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 9) are tabulated below.

Standard solutions:

Nickel standard stock solution	Concentration (ppm)	Procedure
A	1,000	Dissolve 2.48 g nickel nitrate [$Ni(NO_3)_2 \cdot 6H_2O$] in 500 ml of 1:1 nitric acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 1:1 nitric acid.
C	10	Prepare daily by diluting 10 ml of *B* to 100 ml with 1:1 nitric acid.
D	5	Prepare daily by diluting 50 ml of *C* to 100 ml with 1:1 nitric acid.
E	1	Prepare daily by diluting 10 ml of *C* to 100 ml with 1:1 nitric acid.

Working nickel standard solutions (to prepare 50-ml solutions of 1:1 nitric acid containing indicated concentrations of nickel in parts per million, dilute the indicated stock solutions to volume with 1:1 nitric acid):

Concentration	Stock solution
0.2	10 ml of *E*.
0.5	5 ml of *D*.
1	Use *E* above.
3	15 ml of *C*.
5	Use *D* above.

Optimum working range with model 303:
Manual (× 1), 0.2 through 5.0 ppm.
DCR, 0.2 through 5.0 ppm.

Operating conditions for instruments:

	Model 303	*Model 290*
Wavelength (counter)	2320 A	112.5
Source	Hollow cathode	Hollow cathode
Lamp current ma	25	10
Slit	3	2 A
Boling burner:		
Air pressure psi	30	30
Acetylene pressure psi	8	8

Sample digestion: Place 0.5 g of powdered rock or soil in a 16- by 150-mm test tube and proceed as in "General procedure" (p. 9).

Estimation: Refer to "General procedure" (p. 9).

Discussion: The atomic-absorption determination of nickel in silicate rocks is relatively free of interferences provided the iron and calcium contents are not too great (Billings and Adams, 1964; Ragland and Billings, 1965). Molecular absorption by calcium on the nickel line at 2320 A is reported by Billings (1965). A correction can be made on the line at 2325.7 A. P. C. Ragland (cited in Angino and Billings, 1967) observed molecular absorption by iron and calcium on the nickel line during the analysis of granites. As much as 1,000 ppm of several anions—such as sulfate, chloride, phosphate, and nitrate—and cations—such as zinc and lead—did not interfere with the determination of 1 ppm nickel in water samples (Platte and Marcy, 1965).

CALCIUM IN ROCKS, SOILS, AND PLANT ASH, AND LITHIUM, POTASSIUM, AND SODIUM IN ROCKS AND SOILS

GENERAL PROCEDURE

REAGENTS AND EQUIPMENT

Dish, 30 ml, platinum or Teflon.
Flasks, volumetric, 25 ml and 50 ml.
Hydrochloric acid, 6 *M*.
Hydrofluoric acid, 48 percent.
Nitric acid, concentrated.
Perchloric acid, 72 percent.

SAMPLE DIGESTION

Place 0.1 g of powdered rock or soil in 30-ml platinum or Teflon dish and wet sample with 2 ml concentrated nitric acid, 2 ml perchloric acid, and 15 ml hydrofluoric acid. Heat dish gently on hotplate and allow contents to evaporate slowly until dry. Cool dish, add 2 ml 6 *M* hydrochloric acid and heat gently on hotplate to solubilize the residue. Transfer the solution to volumetric flasks as directed under the given procedure.

ESTIMATION

Atomize the aqueous solution in an atomic-absorption spectrophotometer. Read absorbance and refer to standard curves prepared by atomizing portions of working standard solutions to convert to concentration.

INSTRUMENT CALIBRATION

See page 10.

SPECIFIC PROCEDURES

CALCIUM IN ROCKS AND SOILS

The atomic-absorption determination of calcium is relatively easy as shown by the volume of literature describing applications of calcium determinations to a wide variety of materials including geologic. The early studies of Willis (1960a, 1961) on calcium determination in blood serum, urine, and other materials are typical of applications in the clinical laboratory. Calcium determinations in soils and plants by atomic-absorption techniques are described by David (1959) and Dickson and Johnson (1966).

The calcium abundance in rocks and soils is of the order of 0.5–1 percent or more, and the following procedure is designed to detect the lower limit as well as to measure anomalous concentrations. Detection of the lower limit is not a problem because of the good sensitivity of the calcium measurement, 0.8 μg/ml (micrograms per milliliter) for 1 percent absorption. Such sensitivity allows considerable latitude in sample dilution to adjust the calcium content to a convenient level for measurement.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 25) are given below.

Dilution reagent: Mix 90 ml water, 10 ml lanthanum chloride reagent, and 2 ml of 6 *M* hydrochloric acid.

Lanthanum chloride solution: Weigh 58.7 g lanthanum oxide (La_2O_3) into a 100-ml beaker and wet powder with metal-free water. In small portions add 150 ml concentrated hydrochloric acid. When the oxide is completely dissolved, dilute to 500 ml with metal-free water. Dilute slowly with the water while stirring vigorously to avoid overheating.

Standard solutions:

Calcium standard stock solution	Concentration (ppm)	Procedure
A	1,000	Dissolve 2.485 g dried calcium carbonate (overnight at 100°C) in mixture of 40 ml metal-free water and 40 ml 6 *M* hydrochloric acid. Dilute to 1 liter with metal-free water.
B	500	Prepare by diluting 50 ml of *A* to 100 ml with dilution reagent.
C	200	Prepare by diluting 40 ml of *B* to 100 ml with dilution reagent.
D	100	Prepare by diluting 20 ml of *B* to 100 ml with dilution reagent.

Working calcium standard solutions (to prepare 50-ml solutions of dilution reagent containing indicated concentrations of calcium in parts per million, dilute the indicated stock solutions to volume with dilution reagent):

Concentration	Stock solution
10	5 ml of *D*.
40	10 ml of *C*.
60	6 ml of *B*.
80	8 ml of *B*.
100	Use *D* above.
200	Use *C* above.

Operating conditions for model 290:
- 5-cm short-path burner:
  - Air pressure, 30 psi.
  - Acetylene pressure, 8 psi.
  - Burner position:
    - For 0- to 100-ppm and 0- to 200-ppm scales, position burner perpendicular to source beam.
    - For 0- to 10-ppm scale, position burner in line with source beam.
- Counter, 460.
- Source current, 8 ma.
- Slit, 7 A.

Sample digestion: Refer to "General procedure" (p. 25). To the 2 ml of warm hydrochloric acid solution add 5 ml of lanthanum chloride solution and transfer to a 50-ml volumetric flask. Make up to volume with water and mix.

Estimation: Refer to "General procedure" (p. 25).

Discussion: Although calcium is readily determined by atomic-absorption spectrophotometry, the kinds of interference are more numerous and the degree of interference is greater than for most other elements. The interferences encountered especially when analyzing plants and soils are discussed in detail by Dickson and Johnson (1966). They used protective agents such as strontium chloride or lanthanum chloride to nullify the depression of calcium absorption caused by anions such as silicate, phosphate, and sulfate. The standard additions techniques used so successfully in flame emission methods are useful also in atomic-absorption procedures when used in conjunction with protective agents like strontium nitrate (Dickson and Johnson, 1966) to determine calcium in presence of high levels of sulfate and phosphate.

The proposed procedure uses lanthanum chloride to inhibit the interference due to phosphate, sulfate, silicate, and cations such as aluminum. The chloride concentration in the sample solution is reduced to about 0.2 *M*—roughly 700 ppm—and this concentration is below the 1,000 ppm stated by Platte and Marcy (1965) that did not interfere with measurement of 1 ppm calcium in water samples.

CALCIUM IN PLANT ASH

PROCEDURE

Special reagents and equipment, in addition to those listed under "General procedure" (p. 25) and under "Calcium in rocks and soils" (p. 26), are given below.

Flasks, volumetric, 100 ml.

Calcium working standard solutions: See table under "Calcium in rocks and soils" (p. 26).

Sample digestion: Weigh 0.05 g plant ash into 100-ml volumetric flask and add 4 ml 6 *M* hydrochloric acid. Heat on steam bath 20 minutes, remove and add 10 ml lanthanum chloride solution. Dilute to volume with metal-free water and mix.

Estimation: Refer to "General procedure" (p. 25).

LITHIUM IN ROCKS AND SOILS

The abundance of lithium in rocks and soils is of the order of 20–40 ppm, and the sensitivity of about 0.07 ppm for 1-percent absorption achieved under general conditions is more than adequate to detect anomalous concentrations in such materials. With scale expansion one can attain an adequate sensitivity to provide greater latitude in sample dilution.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 25) are given below.

Dilution reagent: Add 20 ml concentrated hydrochloric acid to 1 liter of metal-free water.

Standard solutions:

Lithium standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Dissolve 6.11 g lithium chloride in mixture of 1,000 ml metal-free water and 20 ml concentrated hydrochloric acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with dilution reagent.
C	10	Prepare daily by diluting 10 ml of *B* to 100 ml with dilution reagent.
D	1	Prepare daily by diluting 10 ml of *C* to 100 ml with dilution reagent.

Working lithium standard solutions (to prepare 50-ml solutions of dilution reagent containing indicated concentrations of lithium in parts per million, dilute the indicated stock solutions to volume with dilution reagent):

Concentration	Stock solution
0.5	25 ml of *D*.
1	5 ml of *C*.
2	10 ml of *C*.
10	5 ml of *B*.

Operating conditions for model 290:

5-cm short-path burner:

Air pressure, 30 psi.

Acetylene pressure, 8 psi.

Counter, 953.

Source, hollow cathode.

Lamp current, 5 ma.

Slit, 7 A.

Sample digestion: Place 0.2 g of powdered soil or rock in 30-ml platinum or Teflon dish and proceed as in the "General procedure" (p. 25). After treatment, transfer the 2-ml of warm hydrochloric acid solution to a 25-ml volumetric flask, make up to volume with water, and mix.

Estimation: Refer to "General procedure" (p. 25).

Discussion: Controversy exists regarding possible interferences, especially from sodium and potassium. Zettner, Rafferty, and Jarecki (1968) reported as much as 9-percent enhancement of lithium absorption in solutions containing 50–100 times as much sodium or potassium. Slavin and Slavin (1968) found no more than 3-percent enhancement from solutions containing 250 times as much sodium as lithium. We observed that sodium concentrations of as much as 1,000 ppm caused about 3-percent deflection of meter on a Perkin-Elmer model 290 instrument previously calibrated for 100-percent deflection by 3 ppm lithium solution. Fishman and Downs (1966) reported that more than 5 ppm strontium interfered, but Angino and Billings (1966) were unable to confirm this.

POTASSIUM IN ROCKS AND SOILS

The potassium abundance in soils and rocks is of the order of 1–4 percent and more. The sensitivity of the method described below is about 1 ppm, which is more than needed to measure background concentrations and enough to require several-fold dilution of the sample before measurement of anomalous concentrations.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 25) are given below.

Dilution reagent: Add 20 ml concentrated hydrochloric acid to 1 liter of metal-free water.

Standard solutions:

Potassium standard stock solution	Concentration (ppm)	Procedure
A	1,000	Dissolve 1.92 g potassium chloride in 1,000 ml of dilution reagent.
B	500	Prepare by diluting 50 ml of *A* to 100 ml with dilution reagent.
C	200	Prepare by diluting 40 ml of *B* to 100 ml with dilution reagent.
D	100	Prepare by diluting 10 ml of *A* to 100 ml with dilution reagent.
E	10	Prepare daily by diluting 10 ml of *D* to 100 ml with dilution reagent.

Working potassium standard solutions (to prepare 50-ml solutions of dilution reagent containing indicated concentrations of potassium

in parts per million, dilute the indicated stock solutions to volume with dilution reagent):

Concentration	Stock solution
10	Use *E* above.
20	10 ml of *D*.
40	10 ml of *C*.
80	8 ml of *B*.

Operating conditions for model 290:
- 5-cm short-path burner:
  - Air pressure, 30 psi.
  - Acetylene pressure, 8 psi.
  - Burner position:
    - For 0–10 ppm, burner in line with source beam.
    - For 0–80 ppm, burner perpendicular to source beam.
- Counter, 1169.
- Source, hollow cathode.
- Lamp current, 10 ma.
- Slit, 20 A.

Sample digestion: Refer to "General procedure" (p. 25). After treatment transfer the 2 ml of warm hydrochloric acid solution to a 50-ml volumetric flask, make up to volume with water and mix.

Estimation: Refer to "General procedure" (p. 25).

Discussion: The atomic-absorption determination of potassium is limited by spectral interference from sodium, as noted by Fishman and Downs (1966), Willis (1960b), and Trent and Slavin (1964). The interference is due to ionization and is nullified by equalizing the sodium content of standards and samples (Billings and Harriss 1965). For determining potassium in water, Fishman and Downs (1966) provided easy guidelines to match standards with samples. They found that in samples that contain as much as 1,000 ppm of sodium the effect of the sodium ion on the potassium measurement was constant over a range of ± 50 ppm, and accordingly they added 200 ppm sodium to each standard and then adjusted the sample solution until the sodium ion concentration fell into the range of 150–250 ppm prior to the measurement.

SODIUM IN ROCKS AND SOILS

The atomic-absorption determination of sodium is relatively easy, being limited by its ubiquitous nature and presence in most reagents. The crustal abundance is of the order of 2–4 percent, hence the element

is easily detected by the following procedure that has a sensitivity of at least 0.02 percent. As with potassium, anomalous concentrations of sodium require considerable dilution of sample solution before measurement.

PROCEDURE

Special reagents in addition to those listed under "General procedure" (p. 25) are given below.

Dilution reagent: Add 20 ml concentrated hydrochloric acid to 1 liter of metal-free water.

Standard solutions:

Sodium standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Dissolve 2.54 g sodium chloride in 1,000 ml of dilution reagent.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with dilution reagent.
C	10	Prepare daily by diluting 10 ml of *B* to 100 ml with dilution reagent.

Working sodium standard solutions (to prepare 50-ml solutions of dilution reagent containing indicated concentrations of sodium in parts per million, dilute the indicated stock solutions to volume with dilution reagent):

Concentration	Stock solution
5	25 ml of *C*.
10	Use *C* above.
20	10 ml of *B*.
50	25 ml of *B*.

Operating conditions for model 290:
- 5-cm short-path burner:
  - Air pressure, 30 psi.
  - Acetylene pressure, 8 psi.
  - Burner position:
    - For 0–50 ppm, burner perpendicular to source beam.
    - For 0–5 ppm, burner in line with source beam.
- Counter, 783.
- Source, hollow cathode.
- Lamp current, 10 ma.
- Slit, 7 A.

Sample digestion: Refer to "General procedure" (p. 25). After treatment, transfer the 2 ml of warm hydrochloric acid solution to a 50-ml volumetric flask, make up to volume with water, and mix.

Estimation: Refer to "General procedure" (p. 25).

Discussion: Large amounts of hydrochloric acid, chlorides, and calcium depress the absorbance of sodium according to Rubeska, Moldan, and Valny (1963), but Angino and Billings (1967, p. 54) were unable to find any spectral interferences in determinations of sodium in a calcium carbonate matrix. Both Rubeska, Moldan, and Valny (1963) and Robinson (1960) stated that as much as 3,000 ppm potassium had no effect on the sodium measurements.

In the proposed procedure the sample solution is about 0.2 *M* in hydrochloric acid—much less than that used by Rubeska and coworkers. Presumably this concentration has no depressive effect on the absorbance of sodium.

GOLD, TELLURIUM, AND MERCURY IN ROCKS AND SOILS

SPECIFIC PROCEDURES

GOLD

The three methods presented for atomic-absorption determination of gold in rocks and soils differ mainly in the size of sample taken and the procedure for sample dissolution. In each method the solubilized gold is measured by aspirating the MIBK (methyl isobutyl ketone) extract containing the gold into the flame of an atomic-absorption instrument and comparing the absorbance with that of standards contained in a similar matrix.

The first two methods are described in detail by Thompson, Nakagawa, and VanSickle (1968). Their description includes precision accuracy data, applications of the methods to different geologic materials from several geographic areas and precautions to the analyst to assure reliable results.

The third gold method is given in greater detail by VanSickle and Lakin (1968) including data on the repeatability and reliability of the method. Their report also includes a comparison of gold contents obtained by assay and other methods on different geologic materials including gossan, pyritic rock, and sulfide ore.

The three methods are arranged chronologically in the order of development as the problem of representative sampling became more acute and the need and demand for analytical capability increased.

PROCEDURE, FIRST METHOD

Equipment and reagents are given below.

Culture tubes, screwcap, 25- by 200-mm, with Teflon liner in cap.

Beakers, 50 ml.

Hotplate, oscillating.

Porcelain evaporating dish, 60 mm diameter.
Hydrobromic acid, concentrated, 48 percent.
Hydrobromic acid, 3 *M*—dilute 340 ml concentrated acid to 1 liter with water.
Hydrobromic acid, 1 *M*—dilute 115 ml concentrated acid to 1 liter with water.
4-methyl-2-pentanone (methyl isobutyl ketone) reagent grade.
Sodium bromate ACS.

Standard solutions:

Gold standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Dissolve 0.1 g gold in mixture of hydrobromic acid and bromine and heat gently to expel excess bromine. Cool and dilute to 100 ml with concentrated hydrobromic acid.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 3 *M* hydrobromic acid.
C	25	Prepare by diluting 25 ml of *B* to 100 ml with 3 *M* hydrobromic acid.
D	10	Prepare daily by diluting 10 ml of *B* to 100 ml with 3 *M* hydrobromic acid.
E	5	Prepare daily by diluting 50 ml of *D* to 100 ml with 3 *M* hydrobromic acid.

Working gold standard solutions:

To prepare 50-ml solutions of MIBK containing indicated concentrations of gold in parts per million, add indicated amounts of stock solutions to 30 ml of 3 *M* hydrobromic acid in 125-ml separatory funnel. Add 10 ml MIBK, stopper, and shake contents for 1 minute. Separate phases and transfer MIBK to 50-ml volumetric flask. Add MIBK to mark, mix, and add 1 ml of 1 *M* hydrobromic acid.

Concentration	Stock solution
0.5	5 ml of *E*.
1	10 ml of *E*.
2	10 ml of *D*.
5	10 ml of *C*.

Optimum working range with model 303:

Manual ($\times$ 1), 0.5 through 5.0 ppm.
($\times$ 5), 0.02 through 0.5 ppm.

DCR, 0.02 through 5.0 ppm.

Operating conditions for model 303:

Wavelength, 2430 A.
Source, hollow cathode.
Lamp current, 14 ma.
Range, ultraviolet.
Slit, 4.
Boling burner:
Air pressure, 20 psi.
Acetylene pressure, 8 psi.

Sample digestion: Ignite 2.0 g of powdered rock or soil in porcelain evaporating dish for 10 minutes over Meker burner or until sulfides and organic matter are completely oxidized. Transfer sample to 50-ml beaker and add 0.5 g sodium bromate. Mix sample and bromate thoroughly and add 15 ml concentrated hydrobromic acid. Place beaker and contents on oscillating hotplate and boil until about 5 ml of acid remains. Transfer entire contents of beaker (unattacked sample and acid) to a 25- by 200-mm screwcap tube, wash beaker with several portions of water, and add water to sample solution in the screwcap tube. Make up volume of solution in tube to 35 ml with water. Add 10 ml MIBK and vigorously shake contents of tube for 1 minute. Allow tube to stand until layers separate or centrifuge to accomplish separation. If upper layer is colored, transfer it to clean tube containing 25 ml 1 *M* hydrobromic acid and shake tube and contents for 15 seconds. Repeat if necessary until organic layer is colorless or color ceases to change.

Estimation: Zero instrument with MIBK and atomize the supernatant liquid of each working gold standard solution in the atomic-absorption instrument. Read absorbance or calculate from the percentage of absorption as directed under "Instrument calibration" (p. 10). Set up standard curve or calibrate the instrument as directed under "General procedure" (p. 9). Atomize the organic layer in the atomic-absorption spectrophotometer. Read the absorbance and convert to concentration as directed above for the particular instrument.

PROCEDURE, SECOND METHOD

Reagents other than listed under first method (p. 33) are given below.

Hydrobromic acid, 0.1 *M:* Dilute 25 ml concentrated acid to 2 liters with metal-free water.

Hydrobromic acid-bromine reagent: Add 10 ml bromine, sp gr 3.1, to 2 liters of concentrated hydrobromic acid.

Standard solutions:

Gold standard stock solution	Concentration (ppm)	Procedure
A	1, 000	Prepare as in method 1.
B	100	Prepare as in method 1.
C	20	Prepare by diluting 20 ml of *B* to 100 ml with 3 *M* hydrobromic acid.
D	10	Prepare as in method 1.
E	1	Prepare daily by diluting 10 ml of *D* to 100 ml with 3 *M* hydrobromic acid.

Working gold standard solutions:

To prepare 100-ml solutions of MIBK containing indicated concentrations of gold in parts per million, add indicated amounts of stock solutions to mixtures of 10 ml hydrobromic acid-bromine reagent and 20 ml of metal-free water in 125-ml separatory funnel. Add 10 ml MIBK, stopper, and shake contents for 1 minute. Separate phases and transfer MIBK to 100-ml volumetric flask. Add MIBK to mark, mix, and add 1 ml of 1 *M* hydrobromic acid.

Concentration	Stock solution
0.1	10 ml of *E*.
1	10 ml of *D*.
2	10 ml of *C*.

Operating conditions for model 290:

Counter, 134.5.

Source, hollow cathode.

Lamp current, 5 ma.

Slit, 7 A.

Boling burner:

Air pressure, 30 psi.

Acetylene pressure, 8 psi.

Sample digestion: Ignite 10 g of powdered rock or soil in porcelain evaporating dish for 10 minutes over Meker burner or until completely oxidized. Stir occasionally during ignition. Transfer sample to 25- by 200-mm screwcap tube and carefully add 20 ml of hydrobromic acid-bromine reagent. Cap tube and shake it for 15 minutes. Add 20 ml metal-free water and 10 ml MIBK. Cap tube and shake it again for 3 minutes. Centrifuge tube until layers separate and transfer MIBK to clean tube containing 30 ml 0.1 *M* hydrobromic acid. Shake latter tube for 20 seconds and allow phases to separate.

Estimation: Refer to estimation under "Procedure, first method" (p. 35).

Discussion: The solubility of MIBK in hydrobromic acid increases with concentration of the latter; if the decrease in volume of the ketone is appreciable during extraction, additional ketone is added to correct for apparent loss. H. W. Lakin and G. H. VanSickle (oral commun., 1968) observed that with radioactive gold despite such losses of MIBK during extraction all the gold was in the separated ketone.

Infrequently a side reaction occurs when the solubilized gold is extracted into MIBK from 3–4 *M* hydrobromic acid; this reaction causes the organic layer to sink to the bottom of the screwcap tube. The odor of the heavy organic layer strongly suggests bromoform. If such a side reaction occurs, the analyst should continue as directed in the procedure but should make necessary modifications to transfer the bottom layer instead of the upper layer to a clean tube containing 0.1 *M* hydrobromic acid.

All three procedures for gold include washing the MIBK containing the gold with dilute (0.1 *M*) hydrobromic acid to remove traces of iron which may interfere in the atomic-absorption measurement. The procedure for tellurium requires 1.0 *M* hydrobromic acid in place of the weaker acid above.

PROCEDURE, THIRD METHOD

Equipment and reagents other than listed under first and second methods (pp. 33, 35) are given below.

Furnace, muffle, optional. Ignition over open flame may be substituted.
Jars, glass, 6-oz. Teflon liner in caps.
Bromine, reagent-grade.
Ethyl ether, reagent-grade. Caution! See Ward, Lakin, Canney, and others (1963, p. 5).
Hydrobromic acid, 1.5 *M*. Dilute 170 ml concentrated acid to 1 liter with water.

Standard solutions:

Gold standard stock solution	Concentration ppm	Procedure
A	1, 000	Prepare as in method 1.
B	100	Prepare by diluting 10 ml of *A* to 100 ml with 1.5 *M* hydrobromic acid.
C	10	Prepare fresh by diluting 10 ml of *B* to 100 ml with 1.5 *M* hydrobromic acid.
D	5	Prepare fresh by diluting 50 ml of *C* to 100 ml with 1.5 *M* hydrobromic acid.
E	1	Prepare fresh by diluting 10 ml of *C* to 100 ml with 1.5 *M* hydrobromic acid.

Working gold standard solutions:

To prepare 50-ml solutions of MIBK containing indicated concentrations of gold in parts per million, add amounts of stock solutions given below to 20 ml of 1.5 *M* hybrobromic acid in 100-ml volumetric flask. Add 50 ml of MIBK, stopper, and shake flask for 1 minute.

Concentration	Stock solution
0.1	5 ml of *E*.
0.5	5 ml of *D*.
1	10 ml of *D*.
2	10 ml of *C*.

Operating conditions: Refer to "Procedure, second method" (p. 35).

Sample digestion:

1. Weigh 100 g of sample ground to −100 mesh and transfer it to a porcelain dish. Place dish in a muffle furnace and heat at 700°C for 2 hours.
2. Cool and transfer the sample to a 6-oz glass jar. Add 1 ml bromine and 5 ml ethyl ether. Cap the jar tightly and shake vigorously to mix. Allow jar to stand for about 1 hour and shake it intermittently.
3. Add 20 ml MIBK to mixture. Cap and shake vigorously to mix. Add more MIBK if necessary until the sample is completely wet and has the consistency of a soft mud ball.
4. Remove the cap and add approximately 10 ml 0.1 *M* hydrobromic acid to contents. Stir gently with a porcelain spatula. Continue to add 0.1 *M* acid in small increments and stir until MIBK is separated.
5. Pour off the MIBK into a 25- by 200-mm screwcap culture tube containing 25 ml 0.1 *M* hydrobromic acid. Cap the tube and shake it for 30 seconds.

Estimation: Aspirate the separated organic phase into an atomic-absorption spectrophotometer. Read the percent absorption and convert to concentration as directed for the particular instrument. The gold content, in parts per million, of the sample is equal to:

$$\frac{\mu g/ml \times (ml\ MIBK + ml\ ethyl\ ether)}{100}$$

TELLURIUM

The following procedure is described in detail by Nakagawa and Thompson (1968).

The sensitivity of the method as described here is of the order of 0.2 ppm, and such a sensitivity is barely adequate to measure background concentrations. Thus some kind of preconcentration is required.

Chakrabarti (1967) concentrated tellurium by coprecipitation with elemental arsenic or by forming a complex ion such as potassium hexaiodotellurate or tellurium diethyldithiocarbamate and extracting the complex ion into an immiscible solvent like methyl isobutyl ketone. The following procedure includes a solvent extraction step to enrich the tellurium to a threshold level.

PROCEDURE

For reagents, see "Procedure, first method" under "Gold" (p. 33). Reagents needed in addition to those listed above are given below.

Bromine, reagent-grade.

Hydrobromic acid-bromine reagent. Add 5 ml bromine to 1 liter concentrated hydrobromic acid.

Standard solutions:

Tellurium standard stock solution	Concentration (ppm)	Procedure
A	100	Dissolve 0.0625 g tellurium dioxide in 500 ml concentrated hydrobromic acid.
B	10	Prepare by diluting 10 ml of *A* to 100 ml with 3 *M* hydrobromic acid.
C	5	Prepare by diluting 50 ml of *B* to 100 ml with 3 *M* hydrobromic acid.
D	0. 5	Prepare by diluting 10 ml of *C* to 100 ml with 3 *M* hydrobromic acid.

Working tellurium standard solutions:

To prepare 25-ml solutions of MIBK containing indicated concentrations of tellurium in parts per million, add indicated amounts of stock solutions to 45 ml 3 *M* hydrobromic acid in 100-ml volumetric flask. Add 25 ml MIBK, stopper, and shake flask for 1 minute.

Concentration	Stock solution
0.1	5 ml of *D*.
1	5 ml of *C*.
4	10 ml of *B*.

Optimum working range with model 303:

Manual (× 1), 0.5 through 5.0 ppm.

(× 5), 0.1 through 1.0 ppm.

DCR, 0.1 through 5.0 ppm.

Operating conditions for model 303:
- Wavelength, 214⁰ A.
- Source, hollow cathode.
- Lamp current, 18 ma.
- Range, ultraviolet.
- Slit, 3.
- 10-cm burner:
  - Air pressure, 20 psi.
  - Acetylene pressure, 8 psi.

Sample digestion: Weigh 5 g of sample into a 50-ml beaker and add 20 ml hydrobromic acid-bromine reagent. Place beaker on oscillating hotplate and boil solution gently until the volume of the solution is reduced to approximately 10 ml. Remove beaker from hotplate and allow to cool.

Extraction of tellurium: Transfer entire contents of beaker (acid plus unreacted sample) to a 25- by 200-mm test tube fitted with screwcap. Rinse beaker with three 5-ml portions of water and add rinse portions to tube. Add water to 30-ml mark. Add 10 ml MIBK and shake tube and contents vigorously for 1 minute. Let tube set or centrifuge until the layers separate. If the organic layer is colorless, proceed with estimation below; however, if the organic layer is colored, separate and transfer to a clean screwcap tube containing 25 ml of 1 *M* hydrobromic acid. Cap tube and shake it for 15 seconds. Allow phases to separate and proceed immediately with estimation.

Estimation: Zero instrument with MIBK and atomize the supernatant liquid of each working tellurium standard solution in the atomic-absorption instrument. Read absorbance or calculate from percentage of absorption as directed under "Instrument calibration" (p. 10). Set up standard curve or calibrate the instrument as directed under "General procedure" (p. 9). Atomize the organic extractant into an atomic-absorption spectrophotometer. Repeat and average the readings and convert to parts per million as directed above for the particular instrument.

Discussion: The determination of tellurium by atomic-absorption spectroscopy is much less common than that of other elements described in this publication. In fact, since a sensitivity was first given by Allan (1962), less than a half dozen tellurium analyses have been reported. A reason for such scarcity is implied in one report by Sprague, Manning, and Slavin (1964). They studied among other things the variation of absorbance due to tellurium as a function of lamp current and obtained three different curves with as many hollow-cathode lamps. They also observed severe

interference due to copper lines near the most intense tellurium resonance line, but despite such interferences they were able to establish the optimum conditions for determining tellurium in solution.

Improved technology in hollow-cathode lamp manufacture has largely nullified the copper interference.

Recently, Chakrabarti (1967) reexamined the parameters for atomic-absorption determination of tellurium. He observed a decreased absorption with increased lamp current similar to that observed by Sprague, Manning, and Slavin (1964) and reasoned that the decrease was due to increased Doppler broadening and also to self-absorption broadening of the emitted line from the hollow-cathode source.

Obviously the atomic-absorption determination of tellurium is difficult, and the analyst should exercise extreme care to avoid obvious pitfalls and to develop skills in coping with possible problems like those discussed for gold determinations (p. 37).

MERCURY

The atomic-absorption method described below for determining trace amounts of mercury differs remarkably from other methods given in this report. First, the high volatility and vapor pressure of elemental mercury and several of its compounds simplify the sample dissolution, and second, the ability of the elemental vapor to absorb discrete energy frequencies simplifies the technique of sample introduction into a beam of light. Indeed, such absorption is one of the oldest examples of atomic absorption, and the phenomenon has provided a means of determining mercury qualitatively for nearly a century.

The formation of mercury halos or zones around mercury deposits (Saukov, 1946) and the observed association of mercury with base-metal deposits (Sergeev, 1957) created a demand for reliable quantitative methods for measuring mercury in the parts-per-billion range. The qualitative atomic-absorption method is extremely sensitive, and attempts to make such a method quantitative is a natural step. The success of these attempts is described by Vaughn and McCarthy (1964), Vaughn (1967), and Williston and Morris (1965).

PROCEDURE

Reagents and equipment are given below.

Iron filings, sulfide-free.

Mercury-saturated air. Prepare by placing a few grams of mercury in a 60-ml serum bottle fitted with rubber-membrane stopper.

Mercury-vapor detector. Plans for assembly are given by Vaughn (1967).
Iron sample holders—described by Vaughn (1967).

Weigh or measure by volume a 0.25-g sample of rock or soil ground only enough to pass through a 40-mesh sieve. Place sample into iron sample holder. Cover high-sulfide sample with iron filings. Place sample holder on cam support and raise into upright quartz tube (*b* in fig. 2, Vaughn, 1967). Open bypass cock (exhaust side in diagram of fig. 2, Vaughn, 1967) and heat sample to about 500°C. Allow smoke to pass by amalgamator and out through vent. Change bypass cock to mercury (in fig. 2 of Vaughn, 1967) and switch induction heater to amalgamator (*d* in fig. 2, Vaughn, 1967). Heat amalgamator to maximum reading on the milliammeter or other current-measuring device.

Refer peak current reading to previously established calibration curve to obtain the mercury concentration.

Instrument calibration: By means of a syringe, inject different volumes of mercury-saturated air into the upright quartz tube (*b* in fig. 2, Vaughn, 1967). At a given temperature the mercury-saturated air contains a definite amount of mercury. Prepare calibration curve by plotting the quantities of mercury injected versus the peak currents observed.

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